

PATENT SPECIFICATION

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(54) NEW POLYAMIDES

(71) We, TEIJIN LIMITED a Japanese Body Corporate of No. 1 Umeda, Kita-ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement—

This invention relates to a process for producing a polyamide having recurring units derived from a methyl-substituted phthalic acid and a diamine, and to the product thereby obtained.

Melt-polymerization is an industrially advantageous method of producing polyamides from monomers.

A polyamide derived from a methyl-substituted phthalic acid and a diamine can be provided, for example, by a method of inter-facial polymerization (for example, British Patent 871,580), or by a method involving preparing a diphenyl ester of an alkyl-substituted terephthalic acid from said substituted terephthalic acid and phenol, and polymerizing said ester and an aliphatic or aromatic diamine in an organic liquid medium at a temperature not higher than the melting point of the resulting polyamide (U.S. Patent 3,379,695). Such a method, however, necessarily suffers from the disadvantages of complicated operation and high cost of production.

Research and development work has shown that the occurrence of gelation is drastic and inevitable in the melt-polymerization of an aprotic dicarboxylic acid having a methyl group and a diamine, and that it is practically impossible to obtain a polyamide having an acceptably high molecular weight. Severe gelation occurs when an attempt is made to melt-polymerise methyl-substituted phthalic acids and diamines to form as polyamides.

We have now found that if a reducing phosphorus acid or a salt or ester thereof is present in the polymerization system during the polyamide-forming melt polymerizations of

methylterephthalic and/or methylisophthalic acid with a diamine, the occurrence of severe gelation can be avoided and a polyamide having a reasonably high molecular weight for the fabrication of shaped articles can be obtained.

The same phosphorus compounds have been added to polyamides for other purposes; the idea of using them to prevent gelation in this particular reaction is believed to be entirely new. Moreover, as shown hereinafter by Comparative Examples, this inhibitory action on gelation cannot be achieved by utilizing certain other phosphorus compounds which are known to be incorporated in other types of polyamides or be present in the polyamide-forming reaction system.

According to the present invention there is provided a process for producing a polyamide which comprises melt-polymerising (a) 85—100 mol % of methylterephthalic and/or methylisophthalic acid, together with a substantially equimolar proportion of a diamine with (b) 15—0 mol % of (i) a dicarboxylic acid other than methylterephthalic and methylisophthalic acids, together with a substantially equimolar proportion of a diamine, or (ii) an aminocarboxylic acid or (iii) a lactam of an aminocarboxylic acid, or a mixture of two or all of (i), (ii) and (iii) in the presence of at least 0.01 mol % based on the recurring carbonamide unit of the polyamide to be formed from components (a) and (b), of a reducing phosphorus acid or an ester or salt of such an acid.

The invention also includes the product obtained by the above process. The product may be a mixture of the polyamide (containing recurring units derived mainly from the methyl-substituted phthalic acid and the diamine) with a product obtained from the phosphorus compound which is assumed to be converted usually into the form of phosphoric acid and/or an organo-phosphoric acid or a derivative of one of these acids. However, if

the phosphorus compound is capable of chemically bonding to the terminal amino group of the resulting polyamide, a part of said compound will be bonded to the ends of the polyamide molecular chain in a manner similar to an end-blocking agent.

For convenience we refer to the product as a polyamide, although it will be understood that it will not necessarily consist wholly of a polyamide but may contain a phosphorus compound (and possibly other additives) in admixture therewith.

The dicarboxylic acid used to form the melt-polymerized polyamide is methylterephthalic acid and/or methylisophthalic acid, optionally with other dicarboxylic acid(s) (or an amino carboxylic acid or lactam) as a comonomer. Methylisophthalic acid has three isomers, 2-methyl isophthalic acid, 4-methylisophthalic acid, and 5-methylisophthalic acid. These methylisophthalic acids may be used singly or in admixture. The preferred isomer for use singly is the 4-methyl one.

Examples of the dicarboxylic acids as a comonomer include C_6 — C_{12} straight chain aliphatic dicarboxylic acids such as adipic acid, azelaic acid, sebacic acid, or dodecanedioic acid; aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, or diphenyldicarboxylic acid; and alicyclic dicarboxylic acids such as hexahydroterephthalic acid, or hexahydroisophthalic acid.

Examples of the other comonomers that can be used in the invention in an amount of less than 15 mol% together with methylterephthalic acid and/or methylisophthalic acid and the diamine are C_6 — C_{12} straight chain saturated omega-aminocarboxylic acids such as aminocaproic acid, aminocyclohexanecarboxylic acid, or aminocyclohexanecarboxylic acid, such as caprolactam, ethanethiolactam, or lauro lactam.

Examples of the diamine used to form the melt-polymerized polyamide composition of this invention are C_6 — C_{12} , preferably C_6 — C_{12} , straight chain aliphatic α,ω -diamines, aliphatic diamines having alkyl groups of 1 to 4 carbon atoms in side chains and having 5 to 12, preferably 6 to 12 carbon atoms in the main chain, piperazine, piperazines substituted by an alkyl group, preferably an alkyl group having 1 to 4 carbon atoms, bis-(para-aminocyclohexyl) methane and compounds of the formula



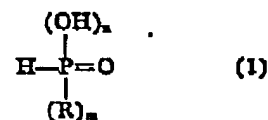
wherein θ is an m-phenylene, p-phenylene, m-cyclohexylene or p-cyclohexylene group, m and n are 1, 2 or 3 when θ is a phenylene group, and 0, 1, 2 or 3 when θ is cyclohexylene. These diamines can be used either singly or in admixtures.

Specific examples of the diamine compo-

nent include tetramethylene diamine, pentamethylene diamine, hexamethylene diamine, heptamethylene diamine, octamethylene diamine, nonamethylene diamine, decamethylene diamine, undecamethylene diamine, dodecamethylene diamine, 2-methylpentamethylene diamine, 2-methylhexamethylene diamine, 3-methylhexamethylene diamine, 3-isopropylheptamethylene diamine, 2-methyl-4-ethylheptamethylene diamine, 2,4-dichyloctamethylene diamine, piperazine, 2-methylpiperazine, 2,5-dimethylpiperazine, 2-ethylpiperazine, 2,5-dichethylpiperazine, 2-isopropylpiperazine, 2-n-butylpiperazine, bis-(para-aminocyclohexyl) methane, meta-xylylenediamine, para-xylylenediamine, 4-aminomethyl, 1-aminocyclohexane, 1,4-bis(aminopropyl)benzene, m-cyclohexylenediamine, p-cyclohexylenediamine, p-aminomethylcyclohexylamine, p-aminopropylcyclohexylamine, and 1,4-bis(aminopropyl)cyclohexane.

Various combinations of the diamine component and the methylterephthalic acid and/or methylisophthalic acid optionally containing another component can be used in the present invention, but it is preferred that the combinations be such that the resulting polyamide has a melting temperature of not higher than 320° C. Furthermore, as a measure of the degree of polymerization, the melt-polymerized polyamide of this invention has a reducing viscosity [η_{sp}/c] (measured at 35° C. in a meta-cresol solution in a concentration of 0.5 g/100 ml.) of 0.7 to 1.6. Preferably, the melt-polymerized polyamide of this invention should be completely soluble in formic acid at 80° C. in a concentration of 1g/100 ml. The solubility of the product as referred to in this invention means this solubility in formic acid.

The preferred phosphorus compounds are acids having the following formula:—

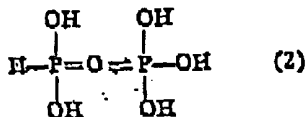


wherein R represents a hydrogen atom, an alkyl group of 1 to 15 carbon atoms, a cycloalkyl group, an aralkyl group, or an aryl group, m is zero or 1, and m+n is 2; esters thereof, and the salts of said acids.

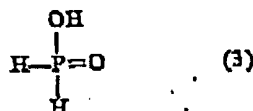
Hereinafter we refer to these acids, esters and salts collectively as "phosphorus compounds" for brevity.

The nomenclature used herein to describe phosphorus compounds is that recommended by the 1952 British and American committees for the nomenclature of phosphorus compounds. It is described in Journal of the Chemical Society 1952, page 5122, and "Phosphorus and its Compounds" by John R.

Van Wazer, Interscience Publishers, Inc., New York, 1958, Volume I, pages 348-351, 387 and 388. In this system of nomenclature the acid of formula (1) above in which $n=2$ and $m=0$ is termed phosphorous acid and has the tautomeric formula



Its monoalkyl, dialkyl and trialkyl esters are termed respectively alkyl phosphonates, dialkyl phosphonates and trialkyl phosphonates. The acid of formula (1) in which $n=1$, $m=1$ and R represents a hydrogen atom is termed hypophosphorous acid and has the formula



Its alkyl esters are termed alkyl phosphinates. The corresponding acids in which R represents a monovalent organic group instead of a hydrogen atom are termed organophosphinic acids. The alkyl esters of such acids are alkyl organophosphinates.

The salts of phosphorous and hypophosphorous acids are termed respectively phosphites and hypophosphites, while the salts of the organo-analogues (in which R=a monovalent organic group) are respectively organophosphonates and organophosphinates.

Readers who refer to the Van Wazer reference for a fuller explanation of this system of nomenclature should note that regrettably there are errors, namely on page 349, Table 7-1, item No. 12, where the 1952 committee name is given incorrectly as "alkylphosphonic acid" instead of the correct name "alkyl phosphonate", and on page 350, Table 7-1, item No. 16, where the 1952 committee name is given incorrectly as "alkyl alkylphosphonic acid" instead of the correct name "alkyl alkylphosphonate".

Examples of the organophosphinic acid are methylphosphinic acid, ethylphosphinic acid, isobutylphosphinic acid, n-propylphosphinic acid, isopropyl phosphinic acid, iso-amylphosphinic acid, n-heptylphosphinic acid, n-octylphosphinic acid, benzylphosphinic acid, cyclohexylphosphinic acid, phenylphosphinic acid, 2-methylphenylphosphinic acid, 3-methylphenylphosphinic acid, 4-methylphenylphosphinic acid, 4-ethylphenylphosphinic acid, 2,4-dimethylphenylphosphinic acid, 2,5-dimethylphenylphosphinic acid, 2,4,5-trimethylphenylphosphinic acid, 2,4,6-trimethylphenylphosphinic acid, 4-isopropylphenylphosphinic acid, 4-phenylphenyl-

phosphinic acid, 4-benzylphenylphosphinic acid, 1-naphthylphosphinic acid, and 2-naphthylphosphinic acid.

The esters are preferably C_1 - C_{10} alkyl, aralkyl or aryl esters of phosphorous, hypophosphorous and organophosphinic acids. Examples of these esters include monoesters such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, iso-amyl, n-octyl, phenyl, 1-naphthyl and 2-naphthyl phosphonates; diesters such as dimethyl, diethyl, di(n-propyl), di(n-butyl), di(n-propyl), di(n-butyl), di(iso-butyl), di(iso-amyl), di(neo-pentyl), di(n-hexyl), di(n-heptyl), dibenzyl, or diphenyl phosphonates; and triesters such as trimethyl, triethyl, tri(n-propyl), tri(iso-propyl), tri(n-butyl), tri(isobutyl), tri(iso-amyl), tri(n-octyl), triphenyl, tri(4-tert-butyl phenyl), tri(2-methylphenyl), tri(3-methylphenyl), tri(4-methylphenyl), tri(1-naphthyl), tri(2-naphthyl), diphenyl propyl, diphenyl butyl, diphenyl 4-tert-butylphenyl and phenyl di(4-tert-butylphenyl) phosphites.

The salts of phosphorous, hypophosphorous and organophosphinic acids are alkali metal salts or are preferably alkali metal or ammonium salts formed between said acids and ammonia or amines. Specific examples include lithium phosphite-monobasic, lithium phosphite-dibasic, lithium hypophosphite, lithium phenylphosphinate, lithium cyclohexylphosphinate, sodium phosphite-monobasic, sodium phosphite-dibasic, sodium hypophosphite, sodium phenylphosphinate, sodium methylphosphinate, sodium ethylphosphinate, sodium cyclohexylphosphinate, potassium phosphite-monobasic, potassium phosphite-dibasic, potassium hypophosphite, potassium phenylphosphinate, potassium cyclohexylphosphinate, ammonium phosphite-monobasic, ammonium phosphite-dibasic, ammonium hypophosphite, ammonium methylphosphinate, ammonium ethylphosphinate, ammonium cyclohexylphosphinate, ammonium phenylphosphinate, ethylene diammonium phosphite, ethylene diammonium hypophosphite, hexamethylene diammonium phosphite, hexamethylene diammonium hypophosphite, hexamethylene diammonium ethylphosphinate, hexamethylene diammonium cyclohexylphosphinate, hexamethylene diammonium phenylphosphinate, piperazine diammonium phosphite, piperazine diammonium hypophosphite, or piperazine diammonium phenyl phosphinate.

In general the proportion of the phosphorus compound will be from 0.01 to 5 mol% based on the recurring carbonamide unit of the resulting polyamide molecular chain. Preferably, the proportion is 0.02 to 4 mol%, and more preferably, at least 0.03 mol% and up to 3 mol%. Since the use of excessively large proportions of phosphorus compound tends to reduce the degree of polymerization of the resultant polyamide, proportions above 5 mol% are not generally beneficial. On the

other hand, if the proportion is less than 0.01 mol%, gelation often cannot be prevented. Therefore, the phosphorus compound should be used in a proportion of at least 0.01 mol%.

The phosphorus compound can be added to the polymerization system at any stage before the last stage of the polymerization. For example, it may be added to the polyamide-forming starting reactants, at the start of the melt-polymerization, at an intermediate stage of the polymerization reaction. In short, it may be added at any time before that at which gelation would otherwise occur, this time being dependent on the reaction conditions and the types of the polyamide-forming reactants, and the type of phosphorus compound. All of the total amount of phosphorus compound required may be added at one time or it may be added in portions, step by step. It is preferred that the phosphorus compound is added before the initiation of the melt-polymerization, at the start of the melt-polymerization, or in a relatively early stage of the polymerization.

Various known polyamide additives can be incorporated in the polyamide of this invention, the examples being a molecular weight regulating agent for polyamides such as acids or amines, stabilizers or antioxidants against heat and/or light, a delustering agent such as titanium dioxide, and various coloring agents.

The melt-polymerized polyamide obtained by the process of this invention is melt-shapable and may have a structure ranging from a crystalline polymer suited for fabrication of shaped articles such as filaments and films to an amorphous polymer which can be used for making ordinary shaped articles.

For example, a melt-polymerized polyamide of good crystallinity can be prepared from 80 to 100 mol% of methylterephthalic acid, 20 to 0 mol% of methylisophthalic acid and a C_6-C_{12} straight-chain aliphatic α,ω -diamine. On the other hand, an amorphous melt-polymerized polyamide can be obtained from 80 mol% to zero mol% of methylterephthalic acid, 20 mol% to 100 mol% of methylisophthalic acid and a C_6-C_{12} straight-chain aliphatic α,ω -diamine or an aliphatic diamine having alkyl group in the side chain in which the main chain has 5 to 12 carbon atoms.

The melt-polymerization can be performed by any known procedures. Usually, by heating the starting materials under a steam pressure at a temperature of 200 to 260° C., the materials are converted to an involatile composition of relatively low molecular weight, and thereafter, the steam pressure is removed. The composition is heated to a temperature above its melting temperature, and then the condensation reaction is caused to proceed.

The melt-polymerized polyamide can be in the form of fabricating materials such as powders, granules or pellets, and also in the form

of filaments, films, and other general fabricated articles.

When the melt-polymerized polyamide of this invention is melt-spun to form filaments, the polyamide is transported in the molten state over a considerable distance from the melting part of the melt-spinning apparatus to the head of the spinning nozzle. However, no gelation of the molten liquid occurs. Even when it stays in the dead point area within the apparatus, the molten polyamide liquid does not form gelled particles there. Accordingly, the polyamide composition of this invention can be melt-spun stably on a continuous basis. Furthermore, the fibers formed thereby are free from defects and of uniform quality.

The invention will be described in greater detail by the following Examples which in no way limit the scope of the present invention. In the Examples, all parts are by weight. The reduced viscosity η_{sp}/c , as a measure of the degree of polymerization, is a value measured in a m-cresol solution in a concentration of 0.5 g polymer/100 ml. of the solution at 35° C. In the following examples, the melt-polymerizing reactor is 18 liters in volume and is equipped with a usual anchor style stirrer which is driven by a 1.5 KW motor.

Examples 1 to 12 and Comparative Examples 1 to 12.

Equimolar proportions of methylterephthalic acid and hexamethylene diamine were dissolved in water to form a salt. By addition of ethyl alcohol, hexamethylene diammonium methylterephthalate was obtained as white powder, which contained one molecule of water of crystallization.

An autoclave equipped with a stirrer was charged with 5,000 parts of hexamethylene diammonium methylterephthalate, 65 parts of stearic acid, and the phosphorus-containing compound shown in Table 1. After replacing the inner atmosphere by nitrogen, the autoclave was closed, and then heated to 260° C. The inner pressure gradually rose with the passage of time, and in 3.5 hours after initiation of heating under stirring, the inner pressure was maintained constant at 15 kg/cm²G. Immediately then, the releasing of the pressure was started, and the heating temperature was raised to 310° C. In the course of about 2 hours, the inner pressure was reduced to 0 kg/cm²G. Then, nitrogen was passed, and heating under stirring was continued at 310° C. for one hour to complete the polymerization. The resulting polymer was extruded into water in the form of a ribbon, and then cut into pellets. The results are shown in Table 1.

For comparison, the foregoing procedure was repeated except that phosphorus com-

pounds outside the scope of this invention were used.

- 5 The resulting pellets were dried to a moisture content of less than 0.01% by weight, and then spun at 315° C. using an extruder-type melt-spinning apparatus (the temperature of the nozzle being 320° C.). The resulting undrawn filaments were drawn to 3 to 4 times the original length using a drawing

machine in which a slit heater held at 250° C. 10 was provided between a hot roller at 140° C. and a roller at room temperature. The spinning conditions and the properties of the drawn filaments are shown in Table 1.

- 15 In Examples 1 to 12, the resulting polyamide had a melting point of 294 to 295° C., and the drawn filaments obtained therefrom had a crystallinity of about 50%.

TABLE 1

Example	Phosphorus compound present in the melt-polymerization system		Gelation during the melt-polymerization	Melt-Polymerized Polyamide Composition Obtained				
	Name	Parts		Solubility (as defined in the specification)	$[\eta]$ (sp/C) (as defined in the specification)	Gelation during melt-spinning	Young's modulus (kg/mm ²)	Properties of the melt-spun filaments Tenacity (g/d) Elongation (%)
1	Phosphorous acid	6.6	None	Completely and uniformly dissolved	1.23	None	920	6.3 15
2	Hypophosphorous acid (50 wt.% aqueous solution)	21.0	"	"	1.18	"	800	5.5 19
3	Ethylphosphinic acid	29.9	"	"	1.02	"	770	4.3 21
4	Cyclohexylphosphinic acid	47.1	"	"	1.07	"	830	4.7 16
5	Phenylphosphinic acid	45.2	"	"	1.06	"	730	4.8 25
6	Diphenyl phosphonate	18.6	"	"	1.28	"	750	5.3 28
7	Trimethyl phosphite	10.0	"	"	1.25	"	910	5.8 16
8	Triphenyl phosphite	24.7	"	"	1.22	"	790	5.5 23
9	Sodium phosphite (dibasic) pentahydrate	17.2	"	"	1.09	"	650	4.2 32

TABLE 1 (continued)

Example	Phosphorus compound present in the melt-polymerization system		Gelation during the melt-polymerization	Melt-Polymerized Polyamide Composition Obtained				
				Solubility (as defined in the specification)	$[\eta]$ (as defined in the specification)	Gelation during melt-spinning	Young's modulus (kg/mm ²)	Properties of the melt-spun filaments Tenacity (g/d) Elongation (%)
10	Ammonium hypophosphite	6.6	None	Completely and uniformly dissolved	1.31	None	1,000	6.1 9
11	Potassium phenylphosphinate	57.3	"	"	0.97	"	890	4.6 12
12	Hexamethylenediammonium phenylphosphinate	41.3	"	"	1.34	"	850	5.4 16
Control	-	-	In 30 minutes after the initiation of polymerization in a nitrogen flow, stirring became impossible, and the polymerization stopped	Only swollen, not dissolved	Not measurable	Not spun judging that the melt-spinning would be impossible	-	- -
Comparative Example 1	Phosphoric acid	15.6	In 35 minutes after the initiation of polymerization in a nitrogen flow, stirring became impossible, and the polymerization stopped	Only swollen, not dissolved	Not measurable	Not spun judging that the melt-spinning would be impossible	-	- -

TABLE I.(continued)

Melt-Polymerized Polyamide Composition Obtained									
Example	Phosphorus compound present in the melt-polymerization system		Gelation during the melt-polymerization	Solubility (as defined in the specification)	[η sp/C] (as defined in the specification)	Gelation during melt-spinning	Properties of the melt-spun filaments		
	Name	Parts					Young's modulus (kg/mm ²)	Tenacity (g/d)	Elongation (%)
Comparative Example 2	Pyrophosphoric acid	28.3	The polymerization could be carried out, but the product could not be taken out from the polymerization reactor in a regular ribbon shape	Partially dissolved	Not measurable	Immediately after initiation of the spinning, the polymer became unflowable at the extruder portion	-	-	-
Comparative Example 3	di(n-octyl)-phosphoric acid (more commonly known as di(n-octyl) orthophosphate).	51.2	In about 40 minutes after initiation of polymerization under nitrogen flow, the stirring became impossible and the polymerization operation stopped	Only swollen, not dissolved	Not measurable	The melt-spinning was stopped, judging that it was impossible	-	-	-
Comparative Example 4	Triphenyl phosphate	51.9	For the same reason as above, the polymerization operation was stopped in about 45 minutes	Only swollen, not dissolved	Not measurable	Ditto	-	-	-
Comparative Example 5	Ammonium phosphate (tribasic)-tribyrate	12.3	For the same reason as above, the polymerization operation was stopped in about 40 minutes	Only swollen, not dissolved	Not measurable	Ditto	-	-	-

TABLE 1 (continued)

Example	Phosphorus compound present in the melt-polymerization system		Gellation during the melt-polymerization	Melt-Polymerized Polyamide Composition Obtained				
	Name	Parts		Solubility (as defined in the specification)	$[\eta]$ (sp/C) (as defined in the specification)	Gellation during melt-spinning	Young's modulus (kg/mm ²)	Properties of the melt-spun filaments Tenacity (g/d) Elongation (%)
Comparative Example 6	Triphenyl phosphine	83.4	For the same reason as above, the polymerization was stopped in about 30 minutes	Only swollen, not dissolved	Not measurable	The melt-spinning was stopped, judging that it was impossible	-	-
Comparative Example 7	Sodium phenylphosphonate (dibasic)	64.2	For the same reason as above, the polymerization was stopped in about 50 minutes	Only swollen, not dissolved	Not measurable	Ditto	-	-
Comparative Example 8	(3,5-ditert. butyl-4-hydroxyphenyl)-methylphosphonic acid	95.2	For the same reason, the polymerization operation was stopped in about 45 minutes	Only swollen, not dissolved	Not measurable	Ditto	-	-
Comparative Example 9	Sodium hexametaphosphate	48.6	The polymerization operation could be carried out, but the product could not be taken out in a regular ribbon shape	Almost uniformly dissolved	0.72	Normal operation of the extruder became impossible after initiation of the spinning	-	-

TABLE I (continued)

Example	Phosphorus compound present in the melt-polymerization system		Gelation during the melt-polymerization	Melt-Polymerized Polyamide Composition Obtained				
	Name	Parts		Solubility (as defined in the specification)	η_{sp}/C (as defined in the specification)	Gellation during melt-spinning	Young's modulus (kg/cm ²)	Properties of the melt-spun filaments Tensile (g/d) Elongation (%)
Comparative Example 10	Triphenylphosphine oxide	88.5	After the initiation of polymerization under nitrogen flow, the stirring became impossible in about 25 minutes	Only swollen, not dissolved	Not measurable	Spinning not performed judging that it would be impossible	-	-
Comparative Example 11	Diphenyl phosphinic acid	69.3	For the same reason, the polymerization operation was stopped in about 30 minutes	Only swollen, not dissolved	Not measurable	Idaho	-	-
Comparative Example 12	Hexamethyl phosphoramide	56.9	For the same reason as above, the polymerization was stopped in about 35 minutes	Only swollen, not dissolved	Not measurable	Idaho	-	-

Except for using the nylon salts indicated in Table 2 instead of hexamethylene diammonium methyl terephthalate, the same procedure as in Control was repeated, and the polyamide obtained was melt-spun under the same conditions as set forth in Examples 1 to 12. The results obtained are shown in Table 2 below.

Comparative Examples 13 to 15. These Comparative Examples will demonstrate that in the melt polymerization for forming polyamides in which methyl-substituted phthalic acids are not the main component of the recurring unit of the polyamide molecular chain, the problem of gelation is not so serious as in the case of preparing polyamide (Control) from methyl-substituted phthalic acids.

TABLE 2

Comparative Examples	Nylon salts	Gelation during melt-polymerization	Melt-polymerized polyamides obtained		
			Solubility	$[\eta]$ sp/C	Gelation during the melt-spinning
13	Hexamethylene diammonium adipate	None	Completely dissolved uniformly	1.32	None
14	Hexamethylene diammonium isophthalate	None	Completely dissolved uniformly	1.38	None
15	A mixture of hexamethylene diammonium adipate (70 mol%) and hexamethylene diammonium terephthalate (30 mol%)	None	Completely dissolved uniformly	1.35	None

Examples 13 to 18.

5 5000 parts of component (a), i.e. a mixture of salts (designated I and II) of a methyl-substituted phthalic acid and diamine were melt-polymerized in the presence of a predetermined amount of each of various phosphorus compounds. Details are set out in Table 3.

10 Specifically, these compounds were heated with stirring for 3.0 hours at 220° C. under a steam pressure. Then, within about 1.5 hours, the inner pressure was reduced down to the normal atmospheric pressure, and the temperature was raised to what is shown as
15 "polymerization temperature" in Table 3.

Subsequently, under a nitrogen stream, the reaction mixture was heated with stirring for 2.0 hours at the "polymerization temperature" to complete the polymerization. For comparison, the above procedure was repeated except that the reducing phosphorus compound was not used (Control). The results obtained are shown in Table 3.

20 The melt-polymerized polyamides obtained in Examples 13 to 18 were transparent thermoplastic resins having a cloud point (as measured in accordance with JIS K-6714) of not more than 10, and have great utilitarian value.

20

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TABLE 3

Examples Nos.	Melt-Polymerization System							Melt-Polymerized Polyamide Composition Obtained			
	Salt I	Mol %	Salt II	Mol %	Phosphorus compound	(parts)	Polymerization temperature (°C)	Solubility	η_{sp}/C	Occurrence of gelation during the polymerization	Temp. at which melting begins (°C)
13	Hexa-methylene diammonium methylterephthalate	60	Hexa-methylene diammonium 4-methylisophthalate	40	Phosphorous acid	10.0	290	Completely dissolved to form a uniform solution	1.56	None	ca. 230
Control	ditto	ditto	ditto	ditto	-	-	ditto	Not dissolved only swollen	Not measurable	In 75 minutes after initiation of polymerization under a nitrogen flow, stirring became impossible, and the polymerization operation was stopped.	-
14	Hexa-methylene diammonium methylterephthalate	20	Hexa-methylene diammonium 4-methylisophthalate	80	Triphenyl phosphite	35.0	270	Completely dissolved to form a uniform solution	1.24	None	ca. 200
Control	ditto	ditto	ditto	ditto	-	-	ditto	Partially dissolved	Not measurable	The above polymerization operation could be carried out, but the product could not be withdrawn from the product	-

TABLE 3 (continued)

Melt-Polymerization System										Melt-Polymerized Polyamide Composition Obtained		
Examples Nos.	Salt I	Mol %	Salt II	Mol %	Phosphorus compound	Amount (parts)	Polymerization temperature (°C)	Solubility	η_{sp}/C	Occurrence of gelation during the polymerization	Temp. at which melting begins (°C)	
15	Hexa-methylene diammonium methylterephthalate	40	Hexa-methylene diammonium 2-methylisophthalate	60	Ammonium phosphite (dibasic) monohydrate	10.7	280	Completely dissolved to form a uniform solution	1.09	None	ca. 220	
Control	ditto	ditto	ditto	ditto	-	-	ditto	Not dissolved only swollen	Not measurable	In 90 minutes after initiation of polymerization, stirring became impossible, and the polymerization operation was stopped	-	
16	Hexa-methylene diammonium methylterephthalate	50	Hexa-methylene diammonium 5-methylisophthalate	50	Hexa-methylene diammonium phosphite	25.0	300	Completely dissolved to form a uniform solution	1.41	None	ca. 235	
Control	ditto	ditto	ditto	ditto	-	-	ditto	Not dissolved, only swollen	Not measurable	In 50 minutes after initiation of polymerization under a nitrogen flow, stirring became impossible, and the polymerization operation was stopped	-	

TABLE 3 (continued)

Examples Nos.	Melt-Polymerization System						Melt-Polymerized Polyamide Composition Obtained				
	Salt I	Mol %	Salt II	Mol %	Phosphorus compound	Amount (parts)	Polymerization temperature (°C)	Solubility	η_{sp}/C	Occurrence of gelation during the polymerization	Temp. at which melting begins (°C)
17	3-Methyl-hexamethylene diammonium methylterephthalate	75	3-Methyl-hexamethylene diammonium 4-methylisophthalate	25	Phenylphosphinic acid	45.2	280	Completely dissolved to form a uniform solution	1.36	None	ca. 215
Control	ditto	ditto	-	-	-	-	ditto	Not dissolved, only swollen	Not measurable	In 90 minutes after initiation of polymerization under a nitrogen flow, stirring became impossible and the polymerization was stopped	-
18	3-Methyl-hexamethylene diammonium methylterephthalate	60	2,5-Dimethyl-hexamethylene diammonium 4-methylisophthalate	40	Hypophosphorous acid	11.0	260	Completely dissolved to form a uniform solution	1.28	None	ca. 190
Control	ditto	ditto	ditto	ditto	-	-	ditto	The insoluble component partly remained	Not measurable	The polymerization operation could be carried out, but the product could not be withdrawn in a regular ribbon shape from the polymerization kettle.	-

Examples 19 to 24.

5 5000 parts of component (a), i.e. a salt of a methyl-substituted phthalic acid and a diamine or mixture of such salts, or, in Examples 23 and 24 only, a mixture of component (a) with component (b), i.e. a salt of a dicarboxylic acid other than a methyl-substituted phthalic acid and a diamine in Example 23 and a lactam in Example 24, were melt-

10 polymerised in accordance with Example 1 in the presence of a predetermined part of each of various phosphorus compounds, and 65 parts of stearic acid as a molecular weight regulating agent. Details are set out in Table

15 4.

20 Specifically, these compounds were heated with stirring at 240° C. under a steam pressure for 3.0 hours. Within about 1.5 hours, the inner pressure was reduced down to normal atmospheric pressure, and simultaneously, the heating temperature was raised to what is shown as "polymerization temperature" in Table 4. Under a nitrogen stream, the heat-

ing of the reaction mixture was continued with stirring for 2.0 hours at the "polymerization temperature", to complete the polymerization. For comparison, the above procedure was repeated except that the reducing phosphorus compound was not used (Control). The results of the polymerization are shown in Table 4.

The resulting polyamides in pellet form were spun in the same way as set forth in Example 1 except using different temperatures. The undrawn filaments obtained were drawn using the same drawing machine as used in Example 1 to make drawn filaments.

The spinning conditions and the properties of the drawn filaments obtained are shown in Table 4 also. The "maximum draw ratio", as referred to in Table 4 means the maximum draw ratio which permits smooth drawing without filament breakage. Usually, the greater this value is, the better the drawability is, and the better the properties of the drawn filaments are.

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TABLE 4

Examples Nos.	Component (a)	Mol %	Component (b)	Mol %	Reducing phosphorus acid compound	Amount (parts)	Polymerization temperature (°C.)	Solubility
19	Hexamethylene diammonium methylterephthalate (85 mol %); hexamethylene diammonium 4-methylisophthalate (15 mol %)	100	—	—	Triphenyl phosphite	33.0	300	Completely dissolved to form a uniform solution
Control	ditto	100	—	—	—	—	ditto	Not measurable
20	Nonamethylene diammonium methylterephthalate	100	—	—	Phosphorous acid	7.7	240	Completely dissolved to form a uniform solution
Control	ditto	100	—	—	—	—	ditto	Almost dissolved

TABLE 4 (Continued)

Examples Nos.	η_{sp}/C	Occurrence of gelation during polymerization	Spinning temperature (°C)	Condition of spinning	Maximum draw ratio	Tenacity (g/den)	Elongation (%)	Young's modulus (kg/cm ²)	Melting point (°C)
19	1.24	None	300	Good	3.8	4.1	21	750	276
Control	Not measurable	In about 50 minutes after initiation of polymerization under a nitrogen flow, stirring became impossible, and the polymerization operation was stopped	-	-	-	-	-	-	-
20	1.08	None	240	Good	4.8	4.0	25	620	207
Control	0.87	The polymerization could be carried out but the product was difficult to withdraw in a regular ribbon shape from the reactor.	Ditto	The spun filaments had rubber elasticity, and the spinnability was poor. Hence, the spinning operation had to be interrupted frequently.	1.7	1.3	16	640	192

TABLE 4 (Continued)

Examples Nos.	Component (a)	Mol %	Component (b)	Mol %	Reducing phosphorus acid compound	Amount (parts)	Polymerization temperature (°C)	Solubility	η_{sp}/C
21	Decamethylene diammonium methylene-phthalate	100	—	—	Phosphorous acid	7.4	270	Completely dissolved to form a uniform solution	1.21
Control	ditto	100	—	—	—	—	ditto	Almost dissolved	0.93
22	Dodecamethylene diammonium methylene-phthalate	100	—	—	Phosphorous acid	6.9	260	Completely dissolved to form a uniform solution	1.19
Control	ditto	100	—	—	—	—	ditto	Almost dissolved	0.95

TABLE 4 (Continued)

Examples Nos.	Occurrence of gelation during polymerization	Spinning temperature (°C)	Condition of spinning	Maximum draw ratio	Tenacity (g/de)	Elongation (%)	Young's modulus (kg/mm ²)	Melting point (°C)
21 Control	None	280	Good	4.2	4.8	18	650	243
	The polymerization operation could be carried out, but the product was difficult to withdraw in a regular ribbon shape from the reactor	ditto	No spinability the operation was impossible	-	-	-	-	-
22 Control	None	270	Good	4.5	5.5	21	560	233
	The polymerization could be carried out, but the product was difficult to withdraw in a regular ribbon shape from the reactor	ditto	No spinability the operation was impossible	-	-	-	-	-

TABLE 4 (Continued)

Examples Nos.	Component (a)	Mol %	Component (b)	Mol %	Reducing phosphorus acid compound	Amount (parts)	Polymerization temperature (°C)	Solubility	η_{sp}/C
23	Dodecamethylene diammonium methylterephthalate	86	Hexamethylene diammonium terephthalate	14	Triphenyl phosphite	26.0	270	Completely dissolved to form a uniform solution	1.26
Control	ditto	86	ditto	14	—	—	ditto	Partly dissolved	Not measurable
24	Hexamethylene diammonium methylterephthalate	90	ϵ -caprolactam	10	Triphenyl phosphite	33.0	300	Completely dissolved to form a uniform solution	1.22
Control	ditto	90	ditto	10	—	—	ditto	Not dissolved, only swollen	Not measurable

TABLE 4 (Continued)

Examples Nos.	Occurrence of gelation during polymerization	Spinning temperature (°C)	Condition of spinning	Maximum draw ratio	Tenacity (g/den)	Elongation (%)	Young's modulus (kg/mm ²)	Melting point (°C)
23 Control	None The polymerization operation could be carried out, but the product could not be withdrawn from the reactor	270 -	Good -	4.0 -	4.6 -	19 -	580 -	238 -
24 Control	None In about 45 minutes after initiation of polymerization under a nitrogen flow, stirring became impossible, and the polymerization operation was stopped	310 -	Good -	4.3 -	5.2 -	16 -	780 -	285 -

WHAT WE CLAIM IS:—

1. A process for producing a polyamide which comprises melt-polymerising (a) 85—100 mol% of methylterephthalic and/or methylisophthalic acid, together with a substantially equimolar proportion of a diamine with (b) 15—0 mol% of (i) a dicarboxylic acid other than methylterephthalic and methylisophthalic acids, together with a substantially equimolar proportion of a diamine, or (ii) an aminocarboxylic acid, or a lactam of an aminocarboxylic acid, or a mixture of two or all of (i), (ii) and (iii) in the presence of at least 0.01 mol%, based on the recurring carbonamide unit of the polyamide to be formed from components (a) and (b), of a reducing phosphorus acid or an ester or salt of such an acid.

2. A process according to claim 1, wherein the proportion of the said phosphorus compound is 0.01 to 5 mol%.

3. A process according to claim 1 or 2, wherein the diamine is a C_4 — C_{12} straight-chain aliphatic α,ω -diamine, an aliphatic diamine having an alkyl group in side chains and containing 5 to 12 carbon atoms in the main chain, a piperazine or alkyl-substituted piperazine, a bis-(para-aminocyclohexyl) methane or a compound of the formula



wherein O represents an m-phenylene, p-phenylene, m-cyclohexylene or p-cyclohexylene group; x and y are 1, 2 or 3 when O represents a phenylene group, and are 0, 1, 2 or 3 when O represents a cyclohexylene group.

4. A process according to any one of claims 1 to 3, wherein said methyl-substituted phthalic acid consists of 80 to 100 mol% of methylterephthalic acid and 20 to 0 mol% of methylisophthalic acid, and said diamine is a C_4 — C_{12} straight-chain aliphatic α,ω -diamine.

5. A process according to claim 1, wherein said methyl-substituted phthalic acid consists of 80 mol to 0 mol% of methylterephthalic acid and 20 mol% to 100 mol% of methylisophthalic acid, and said diamine is a C_4 — C_{12} straight-chain aliphatic α,ω -diamine or an

aliphatic diamine having alkyl groups in the side chains and containing 5 to 12 carbon atoms in the main chain.

6. A process according to any one of claims 1 to 5, wherein a component (b) is employed consisting of (i) a C_4 — C_{12} straight-chain aliphatic dicarboxylic acid, aromatic dicarboxylic acid other than a methyl-substituted phthalic acid or an alicyclic dicarboxylic acid, together with a substantially equimolar proportion of a diamine, (ii) a C_4 — C_{12} straight-chain saturated ω -aminocarboxylic acid or (iii) a lactam of a C_4 — C_{12} straight-chain saturated ω -aminocarboxylic acid.

7. A process according to any preceding claim, wherein the phosphorus compound is an acid of the following formula



wherein R represents a hydrogen atom, an alkyl group of 1 to 15 carbon atoms, a cycloalkyl group, an aralkyl group or an aryl group, m is zero or 1, and m+n equals 2; or an ester or salt of such an acid.

8. A process according to claim 7, wherein said ester is a C_1 — C_{12} alkyl ester, aralkyl ester, or aryl ester of said acid.

9. A process according to claim 7, wherein said salt is an alkali metal salt, ammonium salt or amine salt of a said acid.

10. A process according to claim 1 substantially as described in any one of the Examples.

11. The product obtained by a process claimed in any preceding claim, said product comprising a polyamide.

12. A product according to claim 11 in the form of a powder, granules, pellets, or a shaped article.

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